LEACH OF SAND FROM MAGDALEN SILICA SAND INC. TO PRODUCE A GLASS QUALITY PRODUCT

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by

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INTRODUCTION

Canada imports some $2 million worth of sand annually from the U.S.A. There is growing concern about the continuing availability of imported sand at a reasonable price as high grade and easily accessible U.S.A. resources are being depleted.

Several years ago Magdalen Silica Sands Incorporated began investigating the feasibility of exploiting the silica sand resources immediately off the Magdalen Islands shore. Such a deposit potentially could not only offset sand imports but could help to establish a new industry in an underdeveloped region of Canada. Magdalen Silica Sands Inc. requested the assistance of CANMET in assessing this sand resource and have contracted CANMET to develop the technology to exploit the deposit.

The objectives of the contract were broken into two phases as follows:

Phase I: Preliminary bench-scale investigation to establish procedures and conditions, including small-scale acid leaching tests for treating the sand to produce material with 85% recovery and having the following product specifications:

Glass Sand	Foundry Sands
Fe_2O_3 < 0.035%	Al_2O_3 < 0.20%
Al_2O_3 < 0.20%	
Cr < 5 ppm	
Zn < 3 ppm	

Phase II: To treat an estimated 3 to 4 tons of sand to produce 1500 lbs of sand to glass sand specifications and 500 lbs of sand to foundry sand specifications using the most practical and economic flowsheet indicated by Phase I.

The overall project has involved the application of mineral dressing and extractive metallurgy in meeting the specifications for foundry and glass sands. The mineral dressing work has been conducted in the Mineral Processing Laboratory of CANMET. This work demonstrated that the residual iron content of the treated sand exceeded the specified levels (1). Raw sand analysed 0.23% Fe_2O_3 and a flotation product sand contained 0.11% Fe_2O_3. Therefore the Extractive Metallurgy Laboratory was asked to investigate chemical means of removing iron to meet the specifications.

The literature revealed some background in this area. A review paper by Segrove (2) on British practice reveals that the British imported naturally pure sands from Europe (France, Low Countries and Germany) up to around 1935. One flotation operation was used in Sweden (to upgrade sand to glass quality). In Britain, native sands were then treated by the oxalate process starting in 1935. HCl was rejected as a lixiaviant for economic reasons. Later dilute HF in the presence of a reducing agent, sodium hyposulphite was found effective (to reduce ferric iron to ferrous and promote iron removal). Hyposulphite was found to be the best reducing agent over HSO_3, SO_2^{2-}, $S_2O_3^{2-}$ and S^{2-}. H_2SO_4 is not as effective as HF. In the U.S.A. one operation used a 1 W/O H_2SO_4 at 120°C to remove surface iron compounds. Other American operations used an "attrition" or high speed agitation to remove surface impurities followed by flotation. The Russians followed American practice. It must be noted that the HF-hyposulphite process, examples given (3,4), indicates that the feed iron analyses were between 0.04% and 0.058% Fe_2O_3.

In 1951, MacPherson (5) of the Mines Branch reported on a roast-H_2SO_4 leach process to produce high quality silica sand suitable for the manufacture of glass. Roasting was carried out at 980°F for 30 minutes followed by a H_2SO_4 leach at 190°F. Feed Fe_2O_3 was 0.11% and was reduced to 0.02%. A process was developed in Australia (6) to upgrade beach sand ilmenite. Traditionally H_2SO_4 had been used to upgrade crude ilmenite but it was necessary to use strong acid at high temperatures and pressures. In the new process, an oxidation roast was followed by a reduction roast then a leach using dilute HCl at 100°C and atmospheric pressure.

This study undertook to determine the most effective and economic route for the removal of iron to meet the sand product specifications.

RAW MATERIALS

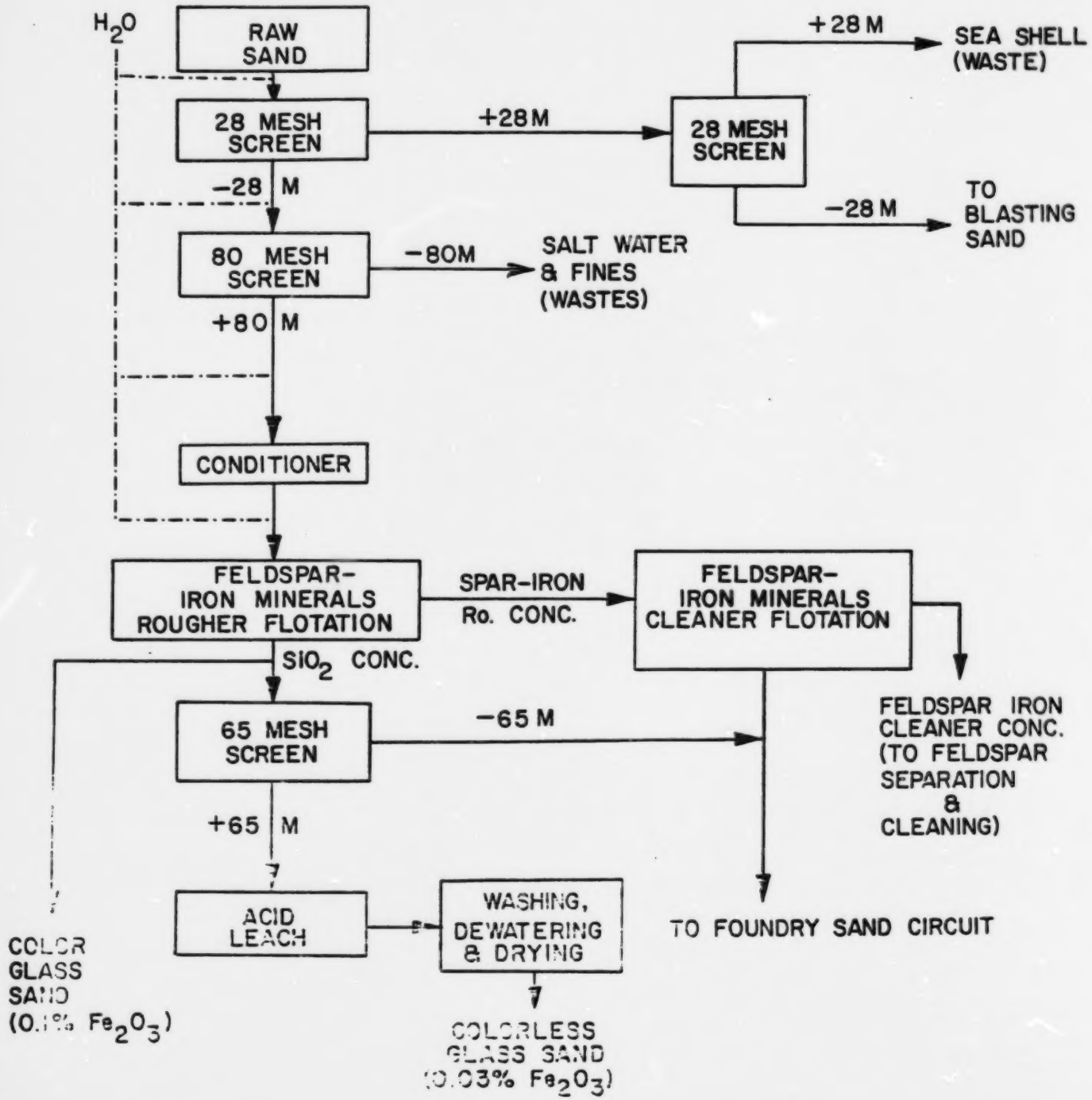
The proposed flowsheet being evaluated to produce foundry and glass sand is shown in Fig. 1. Leach tests were performed on raw sand, flotation sand product (after feldspar removal) and deslimed flotation sand product. The purpose of the leach was to remove the iron contamination. A summary of the mineralogy of the raw sand is shown in Table 1.

Table 1 - Summary of Magdalen sand mineralogy

Product	Minerals	Approx % (overall)
Light fraction Non-Mag (wt ≅ 97%)	Quartz, K-feldspar, Na-feldspar, Ca-feldspar	96+
	ilmenite, rutile (as fine inclusions), chlorite	Trace
	Fe-rich clay mineral (probably as coatings and also ilmenite)	0.1
Light fraction Mag (wt ≅ 2%)	Fe, K, Al, Si clay mineral chlorite	Trace to 0.1%
	Mg, Fe, K, Al, Si biotite	
	Fe, Al, Si peroxine, rutile, ilmenite, hematite	
	Quartz	~2
Heavy mins (wt ≅ 0.2%)	Rutile, ilmenite	Trace to 0.1%
	hematite, Cr-Fe-Al spinel	

From a SEM study, the quartz concentrate contained trace amounts of rutile and chlorite. Some of the quartz grains appeared to be either coated or intergrown with a Fe-rich clay mineral (7). Although Fe_2O_3 and Fe stains would be relatively easy to eliminate by mineral acid dissolution, the minerals like ilmenite, feldspar and clay would necessitate more severe chemical attack.

PROPOSED FLOWSHEET FOR PRODUCING GLASS SAND FROM MAGDALEN SILICA SAND Inc.



LABORATORY BENCH TESTS

Screening of Leaching Agents

In these initial tests a laboratory flotation sand product (after feldspar removal) was leached in several lixiviants, shown in Table 2. The iron concentration in the raw sand had been reduced from 0.23% to 0.11% Fe_2O_3 by flotation and it was thought that dilute leach conditions may be sufficient to reduce the residual iron to the specification limit of 0.035% Fe_2O_3. In Table 2 are the test results from the use of H_2SiF_6, $Na_2S_2O_4$ and H_2SO_4.

Table 2 - H_2SiF_6, $Na_2S_2O_4$ and H_2SO_4 as leaching agents

Test	Leach conditions			% Fe_2O_3	
	% Solids	Temp °C	Time h	Head	Res
1 W/O H_2SiF_6 + 0.2 W/O $Na_2S_2O_4$	50	21	6	0.11	0.047
H_2SO_4 (pH 2.5), 2 W/O $Na_2S_2O_4$	50	70	6	0.11	0.050
35 V/O H_2SO_4 + 1 W/O H_2SiF_6	50	70	6	0.11	0.034
10 V/O H_2SO_4 + excess SO_2	50	70	6	0.11	0.023
10 V/O H_2SO_4 + 2 X STOIC SO_2 for Fe	50	70	6	0.11	0.050

Microscopic observation of the leached sand products indicated some residual iron stain and possibly ilmenite. A concentrated mineral acid and elevated temperature would be necessary to leach the iron sufficiently.

Before further leach tests, a few roast tests were carried out to determine whether the iron species could be made more amenable to dilute leach conditions or converted to water-soluble sulphates. Tests were made using both the raw sand and the sand cleaned by flotation (i.e., 0.23% and 0.11% Fe_2O_3, respectively). The results are given in Table 3.

Table 3 - Roast-leach results

Roast conditions			Leach conditions			% Fe_2O_3	
Time h	Temp °C	Additive %	Time h	Temp °C	Acid	Head	Res
0.5	540	2.5 W/O C	0.25	95	25 V/O H_2SO_4	0.23	0.049
0.5	540	10 V/O SO_2	0.25	95	25 V/O H_2SO_4	0.23	0.066
3.0	390	10 V/O SO_2	0.25	95	25 V/O H_2SO_4	0.23	0.083
3.0	400	10 V/O SO_2	1.0	80	H_2SO_4, pH 1	0.11	0.069
3.0	500	10 V/O SO_2	1.0	80	H_2SO_4, pH 1	0.11	0.061
3.0	600	10 V/O SO_2	1.0	80	H_2SO_4, pH 1	0.11	0.059

SO_2 roasting with a dilute leach had very little effect, but a reduction roast on the head sample had some merit. However, it was felt that if suitable leach conditions could be found, inexpensive H_2SO_4 would be favoured since it could be obtained at a low cost 30 miles from the sand operation.

The preliminary leach tests were completed with a series using HCl and H_2SO_4. The results are found in Table 4. The flotation sand product was used.

Table 4 - HCl and H_2SO_4 leach results

Leach conditions			% Fe_2O_3				
Acid	Temp °C	% Solids	Head	2 h	4 h	6 h	24 h
75 V/O HCl	95	50	0.11	0.017	0.014	0.012	
25 V/O HCl	50	50	0.11	0.048		0.038	0.035
50 V/O H_2SO_4	95	50	0.11	0.078	0.066	0.016	
20 V/O H_2SO_4	50	50	0.11	0.058	0.050		0.049
35 V/O H_2SO_4	70	50	0.11			0.024	

The more extreme conditions indicated that a higher quality glass sand could be obtained if desired. However, intermediate conditions were selected from the H_2SO_4 tests and it was found that 35 V/O H_2SO_4 at 70°C for 6 hours would yield a sand product containing 0.024% Fe_2O_3.

It was obvious that the above amount of H_2SO_4 would have to be recycled to make the process economic. Therefore, a series of ten leach tests, using the flotation sand product, was done using recycled H_2SO_4 at 50% solids. Initial acid strength was 35 V/O and the retention time and temperature 6 hours and 70°C, respectively. The results are shown in Table 5.

Table 5 - Leach tests using recycled H_2SO_4 (35%)

Leach No.	Final % Fe_2O_3	Leach No.	Final % Fe_2O_3
1	0.037	6	0.050
2	0.041	7	0.044
3	0.037	8	0.044
4	0.044	9	0.047
5	0.036	10	0.040

The average from these ten tests was 0.042 % Fe_2O_3. The leach products were then deslimed which gave an average of 0.035% Fe_2O_3. The recycle H_2SO_4 test was repeated using a deslimed flotation sand product as feed which assayed 0.105% Fe_2O_3. The same leach conditions were used but the acid recycled fifteen times. Iron in the final products ranged from 0.022% to 0.043% Fe_2O_3 giving on average of 0.032% Fe_2O_3. There was no trend to increasing iron values as the acid was re-used, indicating that the recycle was effective. No further recycle tests were done to establish the desired bleed.

The option of HCl or H_2SO_4 leaching of the raw sand (0.23% Fe_2O_3) prior to flotation was also evaluated. The results are given in Table 6.

Table 6 - HCl and H_2SO_4 leach of flotation feed sand

Acid	Leach conditions			Final % Fe_2O_3			
	HCl conc'n V/O	% Solids	Temp °C	2 h	4 h	6 h	24 h
HCl	25	50	50			0.16	0.10
	50	50	95	0.058	0.063	0.044	
	75	33	95		0.060		
	75	50	95		0.043		
H_2SO_4*	35	50	70			0.070	

*This test was made on 20 pounds

Further testwork using longer retention time would have to be completed to prove that an acid leach could remove the iron from the raw sand.

It was concluded from the H_2SO_4 and HCl tests that 35% H_2SO_4, 50% solids at 70°C for 6 hours would be sufficient conditions to obtain the desirable iron specifications of 0.035% FeO_3 for glass-quality sand when treating the flotation sand product. Furthermore, it has been found possible to recycle the used H_2SO_4 leach liquor and thus reduce the cost of acid per ton of sand considerably. The above leach conditions were then applied in a pilot plant.

PILOT PLANT

The pilot-plant equipment on hand was limited to polypropylene tanks, peristaltic pumps, rubber hose, rubber-lined thickeners, pumps and rubber-coated impeller due to the severe corrosive conditions created when using 35% H_2SO_4 at 70°C. With the agitation available, slurries were restricted to 50% solids.

One hundred and fifty pounds of deslimed (+65 mesh) flotation sand product were leached in 30 lb lots to prepare samples for evaluation as glass sand feed. Results are shown in Table 7 for the evaluation tests using 35% H_2SO_4, 50% solids at 70°C for 6 hours indicating that specification glass sand could be obtained.

Table 7 - Preparation of glass sand (evaluation sample)

Leach conditions				Feed source	Batch	% Fe_2O_3	
H_2SO_4 conc'n V/O	Temp °C	Time h	Solids %			Head	Residue
35	70	6	50	Lot 2A	A	0.10	0.033
35	70	6	50	Lot 2A	B	0.10	0.032
35	70	6	50	Lot 2A	C	0.10	0.031
35	70	6	50	Lot 1A	-	0.12	0.034
35	70	6	50	Lot 1A	-	0.12	0.034

Samples from the above leaches (Batches A, B, C) were then blended and re-analyzed giving Fe_2O_3 values of 0.027% and 0.028%. The iron results in Table 7 are consistent. The lower analysis values of 0.027% and 0.028% cannot be explained at this time. The average residual Fe_2O_3 value for batches A, B and C is 0.030%.

An attempt was then made to leach on a larger scale (250 lb) in a rubber-lined thickener with rubber-lined diaphragm pumps to recycle the hot acid. However, because the sand was so coarse (+65 mesh) and settled very quickly, the pumps would continually plug. Therefore, further pilot plant leach tests were done in 30 lb lots using a polypropylene-lined tank and a rubber-coated agitator.

The leaching efficiency of recycled 35 V/O H_2SO_4 was evaluated on 12 cycles. Thirty-pounds lots of +65 mesh flotation sand product (0.12% Fe_2O_3) were leached for 6 hours at 70°C. The following results were obtained; in % Fe_2O_3:

0.031, 0.033, 0.042, 0.036, 0.037, 0.037,
0.035, 0.029, 0.041, 0.029, 0.028, 0.042.

The average for the above 12 leaches is 0.035% Fe_2O_3. Again, there is no trend in reduced iron value through the 12 stages. The final leach liquor analyzed 2.73 g Fe^+/L, 1.43 g Al/L and 674 g H_2SO_4/L. To close

out the pilot-plant evaluation of the selected leach conditions, a check was made on the retention time.

A thirty-pound charge of cleaned sand from Mill Run 9-II (Lot 2A) was leached with 35% H_2SO_4, 50% solids at 70°C for 6 hours, and samples taken every hour. The deslimed flotation sand product had a Fe_2O_3 analyses of 0.10%. The following results were obtained:

0.5 hours - 0.063% Fe_2O_3
1.0 hours - 0.047% Fe_2O_3
2.0 hours - 0.036% Fe_2O_3
3.0 hours - 0.037% Fe_2O_3
4.0 hours - 0.033% Fe_2O_3
5.0 hours - 0.035% Fe_2O_3
6.0 hours - 0.034% Fe_2O_3
Final - 0.028% Fe_2O_3

These data indicate that 4-hour retention is sufficient. However, due to possible variation in sand feed iron, leach reproducibility and analytical accuracy, 5-hour retention is recommended.

SPECIAL LEACHES

There are other levels of sand purity required to produce higher quality glasses. Crystal ware sand has an iron specification of 0.013% while optical glass sand must be 0.007%. Sand previously given a H_2SO_4 leach (35% H_2SO_4, 50% solids at 70°C for 6 hours) was subjected to a further 6-hour leach using 75% HCl at 70°C. The following results were obtained:

0.0 - 0.038% Fe_2O_3
0.5 hours - 0.037% Fe_2O_3
1.0 hours - 0.031% Fe_2O_3
2.0 hours - 0.023% Fe_2O_3
3.0 hours - 0.027% Fe_2O_3
4.0 hours - 0.037% Fe_2O_3
5.0 hours - 0.033% Fe_2O_3

6.0 hours - 0.023% Fe_2O_3
Final - 0.028% Fe_2O_3

These leach conditions obviously failed to produce a higher specification product. Leach conditions were revised and test conditions and results are shown in Table 8.

Table 8 - HCl leach tests to product crystal-ware sand

Source	Leach conditions				% Fe_2O_3	
	HCl conc'n %	Temp °C	Time h	Solids %	Head	Residue
H_2SO_4 leached sand	50	95	6	50	0.030	0.022
	75	95	6	50	0.030	0.017

Even under these severe conditions crystal-ware sand purity was not obtained.

WASHING OF LEACHED SAND

Washing of sand after a leach is very difficult as there is a retention of acid on the silica surface. In the laboratory tests, 1% H_2SO_4 was initially used followed by excess water to avoid any iron hydrolysis. Bench-scale wash tests were performed using displacement washing. In 16 displacements of the solution associated with the sand, the pH was only raised to 4.4 using H_2O. In another test, H_2O and 0.5 V/O NaOH was used with the following results indicating less than 0.5% NaOH is necessary.

Wash No.	Wash	pH
1	H_2O	0.19
2	0.5N NaOH	0.52
3	H_2O	8.73
4	H_2O	8.54
5	H_2O	8.53

6	H_2O	8.51
7	H_2O	8.20
8	H_2O	7.83
9	H_2O	7.74
10	H_2O	7.66
11	H_2O	7.32

A series of wash tests was then performed on the pilot plant 30-lb sand lots during the H_2SO_4 recycle runs. The conditions and results are presented in Table 9.

It is evident that the last traces of H_2SO_4 are difficult to remove. Certainly no dilute acid wash step is needed initially. The data in Table 9 does not indicate a relationship between residual iron and washing.

Repulping would use too much water and NaOH. Based on the pH obtained in the final wash water it is recommended that two water displacements be used followed by one displacement using 0.3 W/O NaOH, followed by one H_2O displacement.

DISCUSSION AND CONCLUSIONS

The testwork has demonstrated that sulphuric acid leaching will remove iron from the flotation product to yield sand meeting the 0.035% iron specification. The recommended leach conditions are:

35 V/O H_2SO_4
50% solids
70°C
5-hour retention

The washing should include:

2 displacements using H_2O
1 displacement using 0.3% NaOH
1 displacement using H_2O

Table 9 - Large-scale wash tests - 30-lb batches

Leach Batch #	Wash stages 1	2	3	4	5	6	7	8	9	10	Final wash pH	Batch Sample % Fe_2O_3
1,2,3	3 gal 1 V/O H_2SO_4	3 gal H_2O	3 gal H_2O	3 gal 1 W/O NaOH	3 gal H_2O							0.035
4,5	2 gal 1 V/O H_2SO_4	2 gal H_2O	2 gal H_2O	2 gal 1 W/O NaOH	2 gal H_2O							0.036
6	1 gal 1V/O H_2SO_4	1 gal H_2O	1 gal H_2O	1 gal 1 W/O NaOH	1 gal H_2O						11.4	0.037
7	1 gal H_2O	1 gal H_2O	1 gal H_2O	1 gal H_2O	1 gal H_2O						2.3	0.035
9	5 repulps: 50% solids with H_2O + 5 displac. H_2O										2.8	0.041
10	0.5 gal H_2O	0.5 gal H_2O	0.5 gal 0.1 W/O NaOH	0.5 gal H_2O							1.9	0.029
11	← 0.5 gal H_2O x 8 →								0.5 gal 0.1 W/O NaOH	0.5 gal H_2O	6.2	0.028
12	← 6 x 0.5 gal H_2O, 45°C →						0.5 gal 0.1 W/O NaOH	0.5 gal H_2O			3.3	0.042

The acid was recycled fifteen times in testwork and was still effective. This could be further tested in the plant operation. As of now the estimate, based on 15 recycles; is that 67 lbs H_2SO_4 will be consumed per ton of sand. This would cost 0.67 to $1.34/ton sand. If $Ca(OH)_2$ can be used, the consumption would be about 1 lb $Ca(OH)_2$/ton sand. Therefore, reagent cost will be less than $1.40/ton sand.

It should be noted however that the leach conditions are highly corrosive. Therefore, a production plant should be carefully designed to accomodate such conditions. Polypropylene can be used up to 70°C. Neoprene rubber or possibly chloro-butyl rubber are also resistant. Any unprotected metal would have to be titanium. The sand is quite coarse (-28 mesh +65 mesh) and settles very quickly. However, many sand operations are in existence and therefore suitable tanks, agitation and pumps are availabe to suspend the sand and transfer it. Belt filters may be advisable for filtering and washing. Presumably the wash can be counter current to concentrate the acid displacement in the wash and therefore recycle the first two stages of the wash back to the recycle leach acid for make-up. The NaOH and last H_2O wash would be rejected. Possibly $Ca(OH)_2$ could be used and is much less expensive.

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